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## EVIDENCE OF INORGANIC CHLORINE GASES OTHER THAN HYDROGEN CHLORIDE IN MARINE SURFACE AIR

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**Abstract.** We report the first measurements of inorganic chlorine gases in the marine atmosphere using a new tandem mist chamber method. Surface air was sampled during four days including one diel cycle in January, 1992, at Virginia Key, Florida. Concentrations of HCl\* (including HCl, ClNO<sub>3</sub>, ClNO<sub>2</sub>, and NOCl) were in the range 40 to 268 pptv and concentrations of Cl<sub>2</sub>\* (including Cl<sub>2</sub> and any HOCl not trapped in the acidic mist chamber) were in the range <26 to 254 pptv Cl. Concentrations of Cl<sub>2</sub>\* increased during the night, and decreased after sunrise as HCl\* concentrations increased by similar amounts. The measurements suggest an unknown source of either HOCl or Cl<sub>2</sub> to the marine atmosphere. Photochemical model calculations indicate that photolysis of the observed Cl<sub>2</sub>\* would yield a chlorine atom (Cl•) concentration of order 10<sup>4</sup>–10<sup>5</sup> cm<sup>-3</sup>. Oxidation by Cl• would then represent a significant sink for alkanes and dimethylsulfide (DMS) in the marine boundary layer. The cycling of Cl• could provide either a source or a sink for O<sub>3</sub>, depending on NO<sub>x</sub> levels.

## Introduction

There has been recurring speculation over the years as to the possible role of atomic chlorine (Cl•) in the chemistry of the marine boundary layer [Wofsy and McElroy, 1974; Finlayson-Pitts, 1983; Finlayson-Pitts et al., 1989; Keene et al., 1990]. Singh and Kasting [1988] reviewed the available data on sources of Cl• from (1) oxidation of HCl and CH<sub>3</sub>Cl, (2) photolysis of chlorocarbons, (3) aerosol reactions of ClNO<sub>3</sub>, and (4) reactions of nitrogen oxides on dry NaCl aerosol. They concluded that these processes are too slow to have much effect on the chemistry of the marine boundary layer, although recent work [e.g., Ganske et al., 1992] suggests that reactions involving nitrogen oxides may be more important than estimated by Singh and Kasting [1988]. Here we report preliminary results which indicate the presence in marine surface air of significant concentrations of inorganic chlorine gases other than HCl. Our results suggest a much greater source of Cl• than believed previously.

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## Experimental

Concentrations of inorganic chlorine gases, O<sub>3</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, and black carbon, and size-segregated aerosol ionic composition were measured on the grounds of the NOAA Atlantic Oceanographic and Meteorological Laboratory (AOML), Virginia Key, Miami, FL (see Figure 1). The gas phase chlorine concentration measurements were made during fourteen 2-hour intervals from 22 to 28 January, 1992, using a new tandem mist chamber method described in detail by Keene et al. [1993]. Briefly: After passing through an inertial preseparator to remove coarse particles (>1 μm aerodynamic diameter) and a teflon filter (Zeflour, 2 μm pore diameter) to remove fine particles the chlorine gases were sampled by an acidic mist chamber containing 37.5 mM H<sub>2</sub>SO<sub>4</sub> + 0.042 mM (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> followed by an alkaline mist chamber containing 30.0 mM NaHCO<sub>3</sub> + 0.408 mM NaHSO<sub>3</sub>. Tests with permeation sources indicate that all HCl and a small fraction (<10%) of Cl<sub>2</sub> was sampled by the acidic mist. Results are corrected for the apparent influence from Cl<sub>2</sub>, but ClNO<sub>3</sub>, ClNO<sub>2</sub>, and NOCl may also have contributed to produce Cl<sup>-</sup> in the acidic mist chamber. We, therefore, use HCl\* to denote this chlorine gas. If present, a fraction of HOCl may have been trapped in the acidic mist chamber. Standard additions to mist chamber solutions indicate, however, that HOCl does not generate Cl<sup>-</sup> and is thus not detected by the ion chromatographic analytical technique. The alkaline mist chamber trapped Cl<sub>2</sub> quantitatively and is expected to trap any HOCl remaining in the airstream as well. We use the symbol Cl<sub>2</sub>\* to denote this chlorine. It does not appear that organic chlorine gases are collected in either mist chamber [Keene et al., 1993].

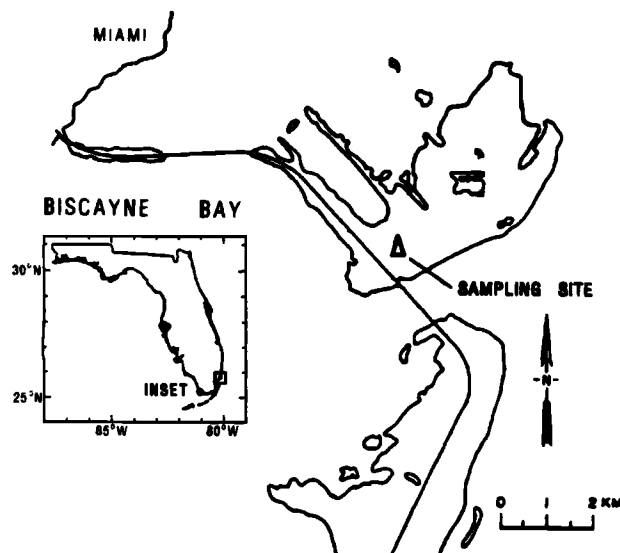


Fig. 1. Location of sampling site on Virginia Key, near Miami, Florida.

Table 1. Meteorological Data and Gas Phase Species Concentrations

Interval	Start† (EST)	End (EST)	T (°C)	R.H. (%)	Wind Direction (degrees)	Wind Speed (m s <sup>-1</sup> )	HCl** (pptv)	Cl <sub>2</sub> ** (pptv Cl)	O <sub>3</sub> ‡ (ppbv)	HNO <sub>3</sub> ‡ (pptv)	SO <sub>2</sub> ‡ (pptv)
<u>22 January 1992</u>											
1	1514	1714	21	80	120	7.5	192	<40	40	<25	140
<u>23 January 1992</u>											
2	0425	0625	22	>98	170	7.	40	26	26	<25	40
3	0651	0851	22	>98	180	8.	63	<26	22	<25	100
4	0921	1122	22	>98	180	7.5	58	<26	19	<25	80
<u>27-28 January 1992</u>											
5	1504	1704	21	85	115	9.5	199	38	37	<30	75
6	1729	1929	21	92	130	9.	150	50	37	<30	100
7	2000	2200	21	93	135	8.5	152	74	36	<30	98
8	2219	0019	21	94	140	8.	146	80	36	<30	76
9	0045	0245	21	94	140	8.	152	206	36	<30	99
10	0308	0508	21	98	140	7.	151	196	36	39	150
11	0530	0731	21	99	150	6.	144	254	34	<30	130
12	0741	0941	22	97	150	6.	187	220	33	<32	76
13	0954	1155	23	91	155	6.	239	152	31	<30	64
14	1205	1405	24	90	160	5.5	268	168	29	15	150

†EST = Eastern Standard Time = UTC - 5 hours.

\*Standard errors: HCl\* ± 20 pptv; Cl<sub>2</sub>\* ± 13 pptv Cl; O<sub>3</sub> ± 1 ppbv; HNO<sub>3</sub> ± 13 pptv; SO<sub>2</sub> ± 20 pptv.

Filter packs were used to collect HNO<sub>3</sub> and SO<sub>2</sub> over 2-hour intervals and cascade impactors were used to collect size-segregated aerosols over 2- or 4-hour intervals following procedures described by Keene et al. [1990]. Concentrations of O<sub>3</sub> were determined by UV photometry [Piotrowicz et al., 1990]. Black carbon concentrations were measured every 5 minutes with an aethalometer [Hansen et al., 1990]. All sampler intakes were mounted on a 10-m scaffolding tower. Vacuum lines connected samplers to air pumps located in a van at the base of the tower.

Meteorological data were recorded with instruments located on the roof of the AOML building. Skies were generally clear with scattered low-level cumulus clouds. Thicker cloud cover and light, widely scattered showers were observed during sampling intervals 3, 4, 5, and 14 (Table 1).

## Results and Discussion

The chemical data are given in Tables 1 and 2. A few measurements on 22-23 January indicate Cl<sub>2</sub>\* concentra-

Table 2. Aerosol Species Concentrations

Interval	NO <sub>3</sub> <sup>-†</sup> (nmol m <sup>-3</sup> )	nss-SO <sub>4</sub> <sup>††</sup> (nmol m <sup>-3</sup> )	NH <sub>4</sub> <sup>††</sup> (nmol m <sup>-3</sup> )	Black Carbon (ng m <sup>-3</sup> )	Coarse Cl <sup>-†</sup> (nmol m <sup>-3</sup> )	Coarse nss-Cl <sup>-†</sup> (nmol m <sup>-3</sup> )
<u>22 January 1992</u>						
1	15±1	5±1	6±2	55	210±3	14±13
<u>23 January 1992</u>						
2+3	7±1	6±1	12±3	110	250±3	10±3
4	6±1	7±1	4±2	190	240±3	-1.6±16
<u>27-28 January 1992</u>						
5+6	18±1	18±1	15±3	92	280±3	1.7±17
7+8	15±1	18±1	16±3	89	320±4	0.9±20
9+10	15±1	No data	14±3	68	220±4	-14±22
11+12	12±1	17±1	14±3	75	260±3	1.4±16
13+14	15±1	16±1	17±3	120	230±3	3.3±14
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Virginia Key, FL (Ref. 1)						
Jan-Mar 1984	45	35	--	--		
Jul-Sept 1984	31	22	--	--		
Subtropical North Atlantic background (Refs. 2 and 3)						
Aug-Sept 1988	3.1	3.4	1.9	140		

†Sum of all 6 cascade impactor stages, nmol m<sup>-3</sup>; non-sea-salt (nss)-SO<sub>4</sub><sup>-</sup> calculated as per Keene et al. [1990].

††Sum of cascade impactor stages 1-4 only (d > ~1 μm); nss-Cl<sup>-</sup> calculated as per Keene et al. [1990].

References: (1) Savoie et al. [1987]; (2) Pszenny et al. [1990]; (3) Hansen et al. [1990].

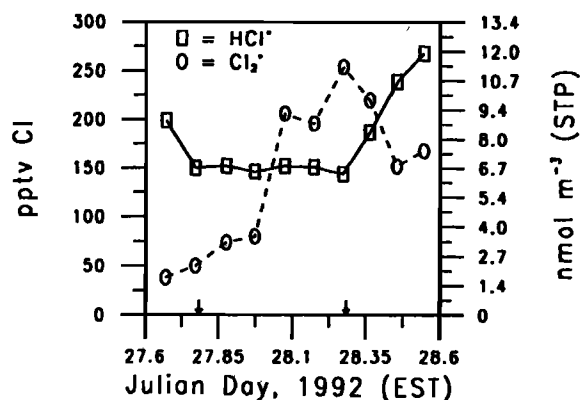


Fig. 2. Diel cycles of  $\text{HCl}^*$  and  $\text{Cl}_2^*$  concentrations in surface air at Virginia Key, 27–28 January, 1992. Data for both species are in units of pptv Cl, and are plotted at midpoints of 2-hour sampling intervals. Sunset and sunrise (marked with arrows) were at 1802 and 0706 EST, respectively.

tions at or below the detection limit. However, measurements over a full diel cycle on 27–28 January indicate substantial concentrations. The  $\text{HCl}^*$  and  $\text{Cl}_2^*$  data for 27–28 January are plotted in Figure 2. During this diel cycle concentrations of  $\text{HCl}^*$  ranged from 144 to 268 pptv Cl with a daytime maximum. Concentrations of  $\text{Cl}_2^*$  ranged from 38 to 254 pptv Cl with a nighttime maximum. The  $\text{Cl}_2^*$  peak just before dawn is consistent with a photolysis sink. The opposite trends in  $\text{HCl}^*$  and  $\text{Cl}_2^*$  during the morning hours suggest that  $\text{HCl}^*$  was produced following the photolysis of  $\text{Cl}_2^*$ .

The chemical data for sea-salt-sized aerosols (Table 2) indicate no significant  $\text{Cl}^-$  deficit like Keene et al. [1990] observed over the open North Atlantic. However, the sums of the observed  $\text{HCl}^*$  and  $\text{Cl}_2^*$  concentrations are smaller than the uncertainties in nss- $\text{Cl}^-$  concentrations, so our data are not inconsistent with a sea-salt origin for the gaseous chlorine.

Local winds during our sampling indicated a predominantly marine fetch (see Table 1 and Figure 1). The observed concentrations of  $\text{HNO}_3$ ,  $\text{SO}_2$  (Table 1) and total aerosol  $\text{NO}_3^-$ , non-sea-salt (nss)  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and black carbon (Table 2) suggest that the air sampled was relatively unpolluted for the locale, but certainly polluted compared to subtropical North Atlantic background. Direct anthropogenic sources for  $\text{Cl}_2^*$  probably were unimportant, however, given the short lifetimes of  $\text{Cl}_2$  and HOCl against photolysis, and the lower concentrations of  $\text{HCl}^*$  and  $\text{Cl}_2^*$  observed on 23 January when Key Biscayne was directly upwind. A chemical source in the atmosphere appears to be needed to explain our observed  $\text{Cl}_2^*$  concentrations.

We examine the potential implications of the measured  $\text{Cl}_2^*$  concentrations using the photochemical box model described by Keene et al. [1990]. The model is applied to a marine surface air parcel containing 200 pptv HCl, 35 ppbv  $\text{O}_3$ , 22 hPa  $\text{H}_2\text{O}$ , 100 pptv  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ), 150 ppbv CO, 1800 ppbv  $\text{CH}_4$ , 2 ppbv  $\text{C}_2\text{H}_6$ , 500 pptv  $\text{C}_3\text{H}_8$ , and 50 pptv DMS, representing relatively clean conditions at northern mid-latitudes in winter. Concentrations of radicals and other secondary species are calculated

assuming chemical steady-state. Photolysis rate constants are calculated with a 6-stream radiative transfer model for the Rayleigh scattering atmosphere, assuming clear sky conditions at noon and an  $\text{O}_3$  column of 270 Dobson units.

Model results are shown in Table 3. In simulation A we compute the steady-state concentrations of gas-phase chlorine species other than HCl by using a standard gas-phase chemistry mechanism with  $\text{HCl} + \cdot\text{OH}$  as the primary  $\text{Cl}\cdot$  source [Singh and Kasting, 1988]. This simulation yields 0.6 pptv HOCl and no  $\text{Cl}_2$ , inconsistent with observed  $\text{Cl}_2^*$  levels and suggesting the need for an additional source of  $\text{Cl}_2^*$ . In simulation B we assume a missing source of  $\text{Cl}_2$  constrained to yield a steady-state  $\text{Cl}_2$  concentration of 100 pptv Cl, representative of observations for  $\text{Cl}_2^*$  on 27–28 January. However, this simulation yields a steady-state HOCl concentration of 134 pptv from the  $\text{ClO}\cdot + \text{HO}_2\cdot$  reaction; thus it would overpredict  $\text{Cl}_2^*$  if HOCl were sampled as  $\text{Cl}_2^*$ . In simulation C we assume a more modest source of  $\text{Cl}_2$  constrained to yield a  $\text{Cl}_2$  concentration of 50 pptv Cl; the resulting steady-state concentration of HOCl is 67 pptv, and the sum ( $\text{Cl}_2 + \text{HOCl}$ ) is 117 pptv Cl. Finally, in simulation D we examine the possibility that the observed  $\text{Cl}_2^*$  may be supplied by a missing source of HOCl constrained to yield a steady-state HOCl concentration of 100 pptv. There is no significant  $\text{Cl}_2$  production in this last simulation.

Results indicate noontime concentrations of  $\text{Cl}\cdot$  in the range  $0.3\text{--}1 \times 10^5 \text{ cm}^{-3}$  for simulations C and D. The  $\text{Cl}\cdot$

Table 3. Results of Photochemical Model Simulations

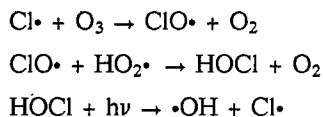
Simulation <sup>†</sup>	A	B	C	D
1. Speciation of chlorine (pptv Cl)				
$\text{Cl}_2$	0.	100.	50.	0.
HOCl	0.6	134.	67.	100.
HCl	200.	200.	200.	200.
$\text{ClNO}_3$	0.4	97.	48.	8.6
2. Required $\text{Cl}_2^*$ source (pptv $\text{Cl h}^{-1}$ )				
	0.	570.	290.	50.
3. Oxidant concentrations ( $\text{molecules cm}^{-3}$ )				
$\text{Cl}\cdot$	$1.4\text{E}3^\ddagger$	$2.6\text{E}5$	$1.4\text{E}5$	$2.8\text{E}4$
$\cdot\text{OH}$	$4.4\text{E}6$	$3.6\text{E}6$	$3.9\text{E}6$	$4.5\text{E}6$
4. Fraction of loss due to oxidation by $\text{Cl}\cdot$				
$\text{CH}_4$	0.005	0.53	0.36	0.087
$\text{C}_2\text{H}_6$	0.073	0.95	0.90	0.61
$\text{C}_3\text{H}_8$	0.036	0.90	0.82	0.43
DMS	0.003	0.44	0.28	0.063

<sup>†</sup>All simulations are for a marine surface air parcel at noon. Simulation A includes  $\text{HCl} + \cdot\text{OH}$  as the primary  $\text{Cl}\cdot$  source; simulation B assumes a missing source of  $\text{Cl}_2$  constrained to yield a  $\text{Cl}_2$  concentration of 100 pptv Cl; simulation C assumes a missing source of  $\text{Cl}_2$  constrained to yield a  $\text{Cl}_2$  concentration of 50 pptv Cl; simulation D assumes a missing source of HOCl constrained to yield a HOCl concentration of 100 pptv Cl.

<sup>‡</sup> $1.4\text{E}3 = 1.4 \times 10^3$ , etc.

concentration is higher in simulation C because the photolysis rate constant of  $\text{Cl}_2$  at noon ( $k = 1.6 \times 10^{-3} \text{ s}^{-1}$ ) is greater than that of  $\text{HOCl}$  ( $k = 1.5 \times 10^{-4} \text{ s}^{-1}$ ). Oxidation by  $\text{Cl}\cdot$  in simulations C and D accounts for significant fractions of the total chemical losses of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , and  $\text{DMS}$ .

Chlorine chemistry also modifies the  $\text{O}_3$  budget in two principal ways. Rapid  $\text{O}_3$  loss takes place by the reaction sequence:



However, this loss can be compensated by enhanced supply of odd hydrogen radicals from the oxidation of alkanes by  $\text{Cl}\cdot$ , leading to  $\text{O}_3$  production in the presence of sufficient  $\text{NO}_x$ . The net effect of chlorine chemistry is thus to increase  $\text{O}_3$  loss at  $\text{NO}_x$  concentrations below about 20 pptv and to stimulate  $\text{O}_3$  production at higher  $\text{NO}_x$  concentrations.

Simulation C requires a  $\text{Cl}_2$  source of  $300 \text{ pptv h}^{-1}$ , while simulation D requires an  $\text{HOCl}$  source of  $50 \text{ pptv h}^{-1}$ . The sources are uncertain, but our data offer a few clues. First, the steady rise of  $\text{Cl}_2^*$  following sunset may indicate a non-photochemical source. Second, the rate of decline of  $\text{Cl}_2^*$  following sunrise suggests a lifetime against photolysis on the order of a few hours, implying that  $\text{HOCl}$  rather than  $\text{Cl}_2$  dominates the  $\text{Cl}_2^*$  pool, at least at night. Improved understanding of chlorine chemistry in the marine boundary layer is evidently needed in view of its potential importance for global atmospheric chemistry.

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